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54 **Epoxy resins containing phosphonium catalysts.**

57 Epoxide compounds and phenolic compounds are reacted in the presence of phosphonium compounds represented by the formula $\ominus Z' R^1 R^2 R^3 P^{\oplus} - Z - P^{\oplus} R^1 R^2 R^3 Z' \ominus$ wherein each R¹, R² and R³ is independently an aromatic group or an inertly substituted aromatic group; Z is $-(C(R^4))_{2a}-$; each R⁴ is independently hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms; Z' is any suitable anion and a has a value of at least 4.

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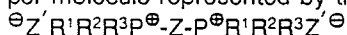
EPOXY RESINS CONTAINING PHOSPHONIUM CATALYSTS

The present invention is directed to epoxy resins containing phosphonium catalysts and a process for reacting epoxy resins with acids and phenolic hydroxyl-containing compounds.

Epoxy resins are well known articles of commerce and are useful in many different applications. Advanced epoxy resins are prepared by reacting a low molecular weight epoxy resin with a polyhydric phenol in the presence of a catalyst. One particularly useful group of catalysts are the phosphonium catalysts as disclosed by Dante et al. in U.S. Patent No. 3,477,990, Perry in U.S. Patent No. 3,948,855, Tyler, Jr. et al. in U.S. Patent No. 4,366,295 and Marshall in U.S. Patent No. 4,634,757. In pre-catalyzed epoxy resin compositions, an ideal catalyst used is one which should be stable at elevated temperatures and which should not become deactivated during prolonged storage at elevated temperatures. In the manufacture of advanced epoxy resins, the ideal catalyst used should also be sufficiently active such that the resultant product reaches its desired target point with respect to its molecular weight or epoxide equivalent weight value, but the catalyst should not be so reactive that the resultant product goes significantly beyond its desired target point with respect to its molecular weight or epoxide equivalent weight. In other words, the ideal catalyst should become essentially deactivated at the resultant products target point. While the catalysts disclosed in the aforementioned patents meet one or more of the above desirable characteristics of an ideal catalyst, none of them meets all of the characteristics of the ideal catalyst.

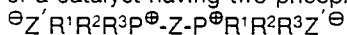
It would be desirable to have a catalyst for the reaction between an epoxide compound and an acidic compound including aromatic hydroxyl-containing compounds which has characteristics which meet or substantially meets the characteristics of the ideal catalyst.

The present invention pertains to a pre-catalyzed composition comprising an epoxy-containing compound having at least one vicinal epoxy group per molecule and a catalyst having two phosphonium groups per molecule represented by the formula



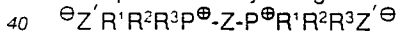
wherein each R^1 , R^2 and R^3 is independently an aromatic group or an inertly substituted aromatic group; Z is $-(C(R^4)_2)_a-$; each R^4 is independently hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms; and Z' is any suitable anion; a has a value of at least 4; and wherein the catalyst is present in an amount of from 0.0005 to 50 milliequivalents per epoxide equivalent contained in the epoxy-containing compound.

The present invention also pertains to a process for reacting an epoxy-containing compound having at least one vicinal epoxy group per molecule with an acidic compound in the presence of a catalytic quantity of a catalyst having two phosphonium groups per molecule represented by the formula



wherein each R^1 , R^2 and R^3 is independently an aromatic group or an inertly substituted aromatic group; Z is $-(C(R^4)_2)_a-$; each R^4 is independently hydrogen or a hydrocarbyl group containing from 1 to 20, more suitably from 1 to 10, most suitably from 1 to 4 carbon atoms; Z' is any suitable anion; and a has a value of at least 4.

In the present invention, the catalyst employed is one which has two phosphonium groups and which can be represented by the general formula



wherein each R^1 , R^2 and R^3 is independently an aromatic group or an inertly substituted aromatic group; Z is $-(C(R^4)_2)_a-$; each R^4 is independently hydrogen or a hydrocarbyl group or inertly substituted hydrocarbyl group containing from 1 to 20, more suitably from 1 to 10, most suitably from 1 to 4 carbon atoms; Z' is any suitable anion and a has a value of at least 4, suitably from 4 to 20, more suitably from 4 to 10, most suitably from 4 to 6.

The term "hydrocarbyl" as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic or cycloaliphatic, or aliphatic or cycloaliphatic substituted aromatic groups. The aliphatic groups can be saturated or unsaturated. The term "inert substituted hydrocarbyl group" means that the hydrocarbyl group can contain one or more substituent groups that does not enter into the reaction and does not interfere with the reaction between the epoxy compound and the compound with which it is being reacted. Suitable such inert groups include, for example, $-CO-Cl$, $-C\equiv N$ and $-OH$.

Suitable anions used in the present invention include, for example, any of those anions described by Dante et al. in U.S. Patent No. 3,477,990, by Perry in U.S. Patent No. 3,948,855, by Tyler, Jr. et al. in U.S. Patent No. 4,366,295 and by Marshall in U.S. Patent No. 4,634,757. Particularly suitable anions include the halides for example, chloride, bromide and iodide and the carboxylates as well as the carboxylic acid

complexes thereof, such as formate, acetate, propionate, oxalate, trifluoroacetate, formate*formic acid complex, acetate*acetic acid complex, propionate*propionic acid complex, oxalate*oxalic acid complex and trifluoroacetate*trifluoroacetic acid complex. Also suitable anions include, for example, phosphate, and the conjugate bases of inorganic acids, such as, bicarbonate, phosphate, tetrafluoroborate or biphosphate and conjugate bases of phenol, such as phenate or an anion derived from bisphenol A.

Some of the catalysts employed in the present invention are commercially available; however those catalysts used in the present invention which are not commercially available can be readily prepared by the method describes by Marshall in the aforementioned U.S. Patent No. 4,634,757. Marshall describes a method for preparing a methylene bis(triphenylphosphonium) dibromide. In the present invention, an appropriate substitute for the methylene bromide employed by Marshall is used in the dihalide which is reacted with the phosphine. Particularly suitable such catalysts include, for example, tetramethylene bis(triphenyl phosphonium chloride), tetramethylene bis(triphenyl phosphonium iodide), tetramethylene bis(triphenyl phosphonium bromide), pentamethylene bis(triphenyl phosphonium chloride), pentamethylene bis(triphenyl phosphonium iodide), pentamethylene bis(triphenyl phosphonium bromide), hexamethylene bis(triphenyl phosphonium iodide), hexamethylene bis(triphenyl phosphonium bromide), heptamethylene bis(triphenyl phosphonium chloride), heptamethylene bis(triphenyl phosphonium iodide), heptamethylene bis(triphenyl phosphonium bromide, tetramethylene bis(triphenyl phosphonium acetate*acetic acid complex), pentamethylene bis(triphenyl phosphonium acetate*acetic acid complex), hexamethylene bis(triphenyl phosphonium acetate*acetic acid complex), heptamethylene bis(triphenyl phosphonium acetate*acetic acid complex), tetramethylene bis(triphenyl phosphonium phosphate), pentamethylene bis(triphenyl phosphonium phosphate), hexamethylene bis(triphenyl phosphonium phosphate), heptamethylene bis(triphenyl phosphonium phosphate), tetramethylene bis(triphenyl phosphonium)bicarbonate, pentamethylene bis(triphenyl phosphonium)bicarbonate, hexamethylene bis(triphenyl phosphonium)bicarbonate, heptamethylene bis(triphenyl phosphonium)bicarbonate, tetramethylene bis(triphenyl phosphonium)oxalate, pentamethylene bis(triphenyl phosphonium)oxalate, hexamethylene bis(triphenyl phosphonium)oxalate, heptamethylene bis(triphenyl phosphonium)oxalate and combinations thereof.

The amount of the catalyst to be employed depends upon the reactants and the products being produced. In any event, the catalyst is employed in an amount sufficient to produce the desired product. When one is reacting a monoepoxide with a monophenol, the amount of catalyst which can suitably be employed is usually from 0.0005 to 50, more suitably from 0.05 to 30, most suitably from 0.5 to 10 milliequivalents of catalyst per epoxide equivalent of the epoxide compound(s). When one is preparing an advanced epoxy resin by reacting a dihydric phenol with a diepoxide, an amount of catalyst corresponding to from 0.0005 to 50, more suitably from 0.005 to 30, most suitably from 0.5 to 10 milliequivalents of catalyst per epoxide equivalent of the epoxide compound(s) is employed. In the precatalyzed composition comprising the polyepoxide and the catalyst, the amount of catalyst is usually from 0.0005 to 50, more suitably from 0.05 to 30, most suitably from 0.5 to 10 milliequivalents of catalyst per epoxide equivalent of the epoxide compound(s).

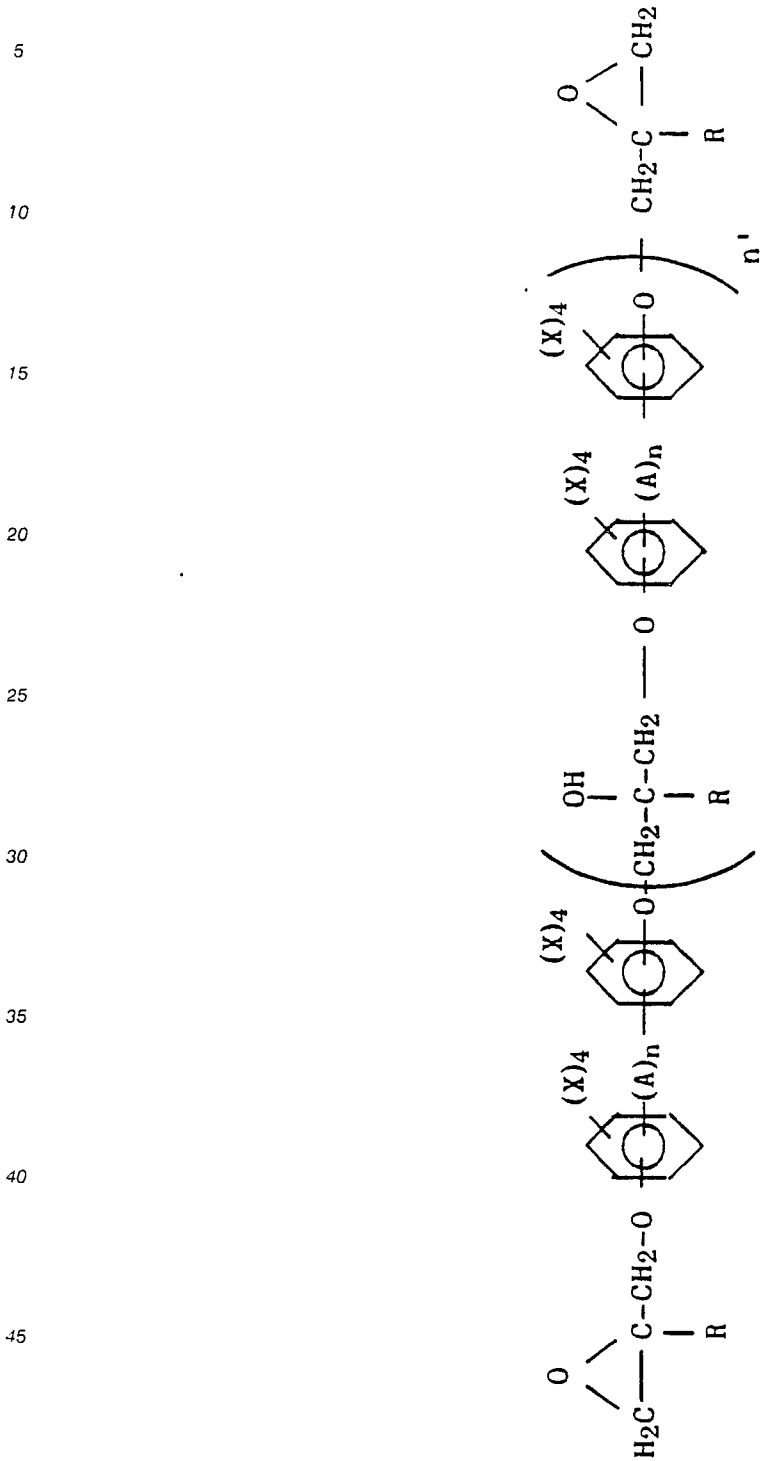
The catalyst can be employed neat or in a solvent which is compatible with the epoxy compound. Particularly suitable such solvents include, for example, alcohols such as, methanol, ethanol, propanol, glycol ethers such as ethylene glycol methyl ether, ethylene glycol n-butyl ether, propylene glycol methyl ether and combinations thereof.

Any vicinal mono- or polyepoxide-containing compounds can be employed herein including the aromatic or aliphatic based mono- and the polyepoxides. Any of the epoxide materials disclosed in the aforementioned U.S. Patents to Dante et al., Perry, Tyler, Jr. et al. and Marshall can also be employed herein.

Suitable monoepoxides which can be employed herein include, for example, the alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, the epichlorohydrins such as epichlorohydrin, epibromohydrin and epiiodohydrin. Also suitable monoepoxides which can be employed are the glycidyl ethers of aliphatic and aromatic alcohols, for example, butyl glycidyl ether and phenyl glycidyl ether.

Suitable polyepoxides which can be employed herein include the diglycidyl ethers of the dihydroxy phenols, for example, resorcinol, catechol and hydroquinone, the diglycidyl ethers of biphenol and bisphenols, for example, bisphenol A, bisphenol F, bisphenol K, bisphenol S, as well as the alkyl and halogen derivatives thereof such as the C₁ to C₄ alkyl, chlorine or bromine derivatives. Also suitable are the polyglycidyl ethers of the novolac resins prepared by reacting a phenol or alkyl or halogen substituted phenol with an aldehyde such as formaldehyde. Suitable also are the polyglycidyl ethers of the adducts of alkadiene or oligomers of alkadienes such as cyclopentadiene and dicyclopentadiene with a phenol or substituted phenol. These are disclosed by Nelson in U.S. Patent 4,390,680. Mixtures of any of the epoxide-containing compounds can be employed. Preferably, the epoxide-containing compounds are the diglycidyl

ethers of dihydroxyl-containing compounds represented by the following formula



wherein A is a divalent hydroxycarbonyl group having from 1 to 12, more suitably from 1 to 8, most suitably from 1 to 4 carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms, preferably hydrogen or methyl, most preferably hydrogen; each X is independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having from 1 to 12, more suitably from 1 to 6, most suitably from 1 to 4, carbon atoms or a halogen, preferably chlorine or bromine; n has a value of zero or 1 and n' has a value from zero to 0.5, more suitably from 0.035 to 0.25, most suitably from 0.03 to 0.1.

Suitable acidic compounds which can be employed herein include, for example, carboxylic acids, anhydrides of carboxylic acids and aromatic hydroxyl-containing compounds as disclosed by the aforemen-

tioned Marshall in U.S. Patent No. 4,634,757. The acids and anhydrides can be unsaturated, saturated, aliphatic, cycloaliphatic, aromatic or heterocyclic. Suitable such acids include, for example, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, oxalic acid, abietic acid, maleic acid, aconitic acid, chlorendic acid, phthalic acid and combinations thereof.

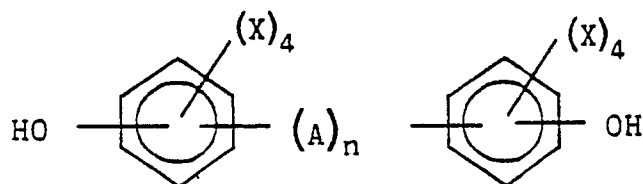
5 Suitable anhydrides include, for example, those which possess at least one anhydride group, i.e., a -CO-O-CO- group. Particularly suitable such anhydrides include, for example, phthalic anhydride, isophthalic anhydride, di-, tri-, tetra- and hexahydrophthalic anhydride, 3,4,5,6,7,7-hexachloro-3,6-endomethylene-1,2-tetrahydrophthalic anhydride (chlorendic anhydride), succinic anhydride, maleic anhydride, maleic anhy-
10 dride, chlorosuccinic anhydride, monochloromaleic anhydride, 6-ethyl-4-cyclohexene-1,2-dicarboxylic acid anhydride, 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylic acid anhydride, 6-butyl-3,5-cyclohexadiene-1,2-dicarboxylic acid anhydride, octadecylsuccinic acid anhydride, dodecylsuccinic acid anhydride, dioctylsuc-
15 cinic acid anhydride, nonadecadienylsuccinic acid anhydride, adducts of maleic anhydride with polyunsaturates such as methylcyclopentadiene (Nadic methyl anhydride) 3-butoxy-1,2,3,6-tetrahydrophthalic acid anhydride, trimellitic acid anhydride, pyromellitic acid anhydride, di-, tetra-, and hexahydropyromellitic acid
15 anhydride, polyadipic acid anhydride, polysebacic acid anhydride and combinations thereof. Derivatives of the anhydrides, such as their partial esters and amides can also be employed. Examples of such derivatives are esters of glycols and pyromellitic acid anhydride, and partial esters of trimellitic acid anhydride.

Particularly suitable aromatic hydroxyl-containing compounds which can be employed herein include monophenols or polyphenols or the alkyl or halogen substituted derivatives thereof. Suitable monophenols
20 which can be employed herein include, for example, phenol, o-, m- and p-cresol, chlorophenol, bromophenol and nitrophenol. Suitable compounds containing two aromatic hydroxyl groups per molecule which can be employed herein include, for example, catechol, resorcinol, hydroquinone, biphenol, bisphenol A, bisphenol F, bisphenol K, and bisphenol S. Suitable compounds having more than one aromatic hydroxyl
25 group per molecule which can be employed herein include, for example, novolac resins which are the acid catalyzed reaction product of a phenol or an alkyl or halogen substituted phenol and an aldehyde, particularly formaldehyde. These novolac resins have an average of from 1.01 to 8, more suitably from 1.01 to 6, most suitably from 1.01 to 4 aromatic hydroxyl groups per molecule. Also suitably employed herein
30 are alkyl and halogen, particularly chlorine and bromine, derivatives of these novolac resins. Suitably employed herein also are adducts of alkadiene or oligomers of alkadienes such as cyclopentadiene and dicyclopentadiene with a phenol or substituted phenol. These are disclosed by Nelson in U.S. Patent No. 4,390,680.

Any of the aromatic hydroxyl-containing compounds disclosed in the aforementioned patents to Dante et al., Perry, Tyler, Jr. and Marshall can suitably be employed herein. The preferred aromatic hydroxyl-
35 containing compounds are those represented by the following formula

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45 wherein A is a divalent hydrocarbyl group having from 1 to 12, more suitably from 1 to 8, most suitably from 1 to 4 carbon atoms; each X is independently hydrogen, halogen, particularly chlorine or bromine, or an alkyl group having from 1 to 6, more suitably from 1 to 4 carbon atoms; and n has a value of zero or 1.

In the reaction between the phenolic hydroxyl-containing compound and the epoxide-containing compounds, the reactants can be employed over a wide range from stoichiometric quantities to an excess of the phenolic compound to an excess of the epoxide compound. The particular amount depends upon the
50 reactants themselves and the type of product desired. If it is desired to prepare large molecular weight materials from diepoxides and diphenols then a stoichiometric quantity, i.e. one phenolic hydroxyl group per epoxide group, of each of the compounds is employed. If it is desirable to have a product which is terminated in phenolic hydroxyl groups, then an excess of the phenolic compound is employed. If it is desirable to prepare a product which is terminated in epoxide groups, then an excess of the epoxide-
55 containing compound is employed. In the preferred embodiment of preparing advanced epoxy resins from diepoxy compounds and diphenols, the reactants are employed in amounts which provide a ratio of phenolic hydroxyl groups per epoxide group of from 0.2:1 to 2:1, more suitably from 0.4:1 to 1.5:1, most suitably from 0.6:1 to 1:1.

The reaction between the phenolic hydroxyl-containing compounds and the epoxide-containing compounds can be conducted in the presence or absence of solvents or diluents. If solvents or diluents are desired to be employed, suitable such solvents or diluents include, for example, aromatic and aliphatic hydrocarbons such as, pentane, hexane, heptane, octane, nonane, decane, benzene, toluene and xylene, 5 alcohols such as methanol, ethanol, isopropyl alcohol and butanol, glycol ethers such as butylene glycol methyl ether, diethylene glycol n-butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, ethylene glycol n-butyl ether, ethylene glycol ethyl ether, ethylene glycol methyl ether, ethylene glycol phenyl ether, propylene glycol phenyl ether, propylene glycol methyl ether and tripropylene glycol methyl ether, amides such as dimethyl formamide, sulfoxides such as dimethyl 10 sulfoxide. Mixtures of any of the solvents in any combination can be employed, if desired.

The reaction between the phenolic hydroxyl-containing compound and the epoxide-containing compound can be conducted at temperatures from 40 °C to 280 °C, suitably from 100 °C to 240 °C, more suitably from 120 °C to 230 °C, most suitably from 130 °C to 220 °C. The reaction can be conducted at any 15 practical pressure which can be subatmospheric to superatmospheric pressure. Usually the reaction is conducted at pressures of from 1 psig to 150 psig, more suitably from 5 psig to 80 psig, most suitably from 10 psig to 20 psig.

The epoxy resins produced by the process of the present invention are useful in all of the applications for which epoxy resins are known, for example, castings, coatings, laminates, composites and encapsulants.

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Examples 1-2 and Comparative Experiments A-G

(Preparation of Advanced Epoxy Resins)

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A series of advanced epoxy resins were prepared by the following procedure employing different catalysts.

30 Into a 1-liter, 5-necked glass reactor equipped with a mechanical stirrer, a thermometer connected to a temperature controller and heating mantle, was charged 395.9 gms (2.075 equivalents) of a diglycidyl ether of bisphenol A liquid epoxy resin having an epoxide equivalent weight (EEW) of 190.8. The reactor was purged with nitrogen and the resin warmed to 80 °C. Bisphenol A, 204.1 gms (1.790 equivalents), was then added and mixed for 15 minutes at 80 °C. The catalyst and catalyst quantity indicated in Table I was added 35 to the resin/bisphenol A slurry and the temperature was gradually increased to 150 °C over a 45 minute period. Heating was turned off at 150 °C and an exotherm was allowed to take place to 190 °C to 200 °C. Air cooling was used to control the exotherm temperature to less than 200 °C. The cook temperature was maintained at 190 °C to 200 °C for 4 hours while samples are taken for product analyses. After reacting for 4 hours, the resin was poured out and flaked on aluminum foil.

40 The catalyst, catalyst quantities and results are given in Table I and II. Comparative analysis results are shown in Table I and catalyst activity data are shown in Table II.

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TABLE I
COMPARATIVE PRODUCT PROPERTIES

Ex. or Comp. Expt.	CATALYST	Amount of Catalyst (milliequiv.)	EEW	% of Target EEW ^a	Viscosity cps (Pa*s)	Weight Average Molecular Weight	Mw/Mn
1	tetramethylene bis (TPhPB ^b)	0.57	2,161	102.9	18,000 (18)	16,226	3.56
2	pentamethylene bis (TPhPB ^b)	0.57	2,139	101.9	16,500 (16.5)	15,043	3.30
A*	methylene bis (TPhPB ^b)	0.57	2,302	109.6	30,000 (30)	19,154	3.80
B*	ethylene bis (TPhPB ^b)	0.57	1,896	90.3	7,000 (7)	11,039	2.92
C*	trimethylene bis (TPhPB ^b)	0.57	2,063	98.2	11,000 (11)	13,066	3.12
D*	1,4-butene bis (TPhPCl ^c)	0.57	1,933	92.0	7,500 (7.5)	11,162	2.88
E*	1,2-vinylene bis (TPhPB ^b)	0.57	1,977	94.1	8,500 (8.5)	11,987	3.01
F*	p-xylylene bis (TPhPB ^b)	0.57	1,853	88.2	5,000 (5)	10,125	2.82
G*	ethyl (TPhPB ^b)	0.57	2,058	98.0	13,000 (13)	13,218	3.17

*Not an Example of the present invention.

^aThe target EEW is 2,100.

^bTPhPB^r is triphenyl phosphonium bromide.

^cTPhPCl is triphenyl phosphonium chloride.

TABLE II

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CATALYST ACTIVITY								
Ex. or Comp. Expt.	CATALYST	% ACTIVE CATALYST AT INDICATED MINUTES AFTER EXOTHERM						
		5	30	60	120	180	240	
1	tetramethylene bis (TPhPBr ^a)	77	65	48	30	21	16	
2	pentamethylene bis (TPhPBr ^a)	70	61	48	34	20	ND ^c	
A*	methylene bis (TPhPBr ^a)	69	67	64	64	56	53	
15	B*	ethylene bis (TPhPBr ^a)	43	25	16	ND ^c	ND ^c	ND ^c
	C*	trimethylene bis (TPhPBr ^a)	53	35	23	ND ^c	ND ^c	ND ^c
	D*	1,4-butene bis (TPhPBr ^b)	46	30	16	ND ^c	ND ^c	ND ^c
20	E*	1,2-vinylene bis (TPhPBr ^a)	71	43	27	18	ND ^c	ND ^c
	F*	p-xylylene bis (TPhPBr ^a)	34	25	ND ^c	ND ^c	ND ^c	ND ^c
	G*	ethyl (TPhPBr ^a)	78	30	13	ND ^c	ND ^c	ND ^c

*Not an Example of the present invention.

^aTPhPBr is triphenyl phosphonium bromide.

^bTPhPBr is triphenyl phosphonium bromide.

^cND is not detectable.

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The data shows that tetramethylene bis triphenyl phosphonium bromide and pentamethylene bis triphenyl phosphonium bromide are superior catalysts, as compared to a conventional catalyst such as ethyl triphenyl phosphonium bromide. Tetramethylene bis triphenyl phosphonium bromide and pentamethylene bis triphenyl phosphonium bromide remained active throughout the reaction and became deactivated only at the end of the reaction, whereas ethyl triphenyl phosphonium bromide was deactivated after only one hour, resulting in an incomplete reaction, lower viscosity, and lower molecular weight products. Methylene bis triphenyl phosphonium catalyst did not become deactivated and continued to build high viscosity and high molecular weight and thus was not suitable for resin advancement. Other evaluated bisphosphonium catalysts showed very poor reactivity and produced very low viscosity, low MW products.

Examples 3-4 and Comparative Experiments H-I

(Pre-Catalyzed Resin Comparison)

A series of precatalyzed epoxy resins were prepared by the following procedure employing different catalysts.

Into a 4 oz. glass bottle was weighed 96.0 gms (0.531 epoxy equiv.) of a liquid diglycidyl ether of bisphenol A having an EEW of 180.7 and 4 gms of xylene. After the epoxy resin/xylene mixture was thoroughly agitated, the catalyst and catalyst amount indicated in Table III was added to the mixture. The pre-catalyzed epoxy resin mixture was then agitated using a mechanical mixer and subjected to heat aging in a convection oven controlled at 90 °C. The catalytic activity of the catalyst remaining after heat aging over a period of time is reported in Table III.

TABLE III

Ex. or Comp. Expt.	Catalyst	Amount of Catalyst (milliequiv.)	% ACTIVE CATALYST AT 90 °C AFTER THE INDICATED TIME AT 90 °C				
			0 hr	6 hrs	24 hrs	48 hrs	72 hrs
3	tetramethylene bis (TPhPBr ^a)	0.45	100	86	69	61	56
4	tetramethylene bis (TPhPP ^b)	0.45	100	98	92	81	79
H*	EtTPhP Acetate • HAc ^c	0.45	100	40	10	8	7
I*	EtTPhP ^d Iodide	0.45	100	87	59	41	30

* Not an example of the present invention.

^a TPhPBr is triphenyl phosphonium bromide. The catalyst is employed as a 16.5% solution in methanol in an amount which provides 0.45 milliequivalent of catalyst.

^b TPhPP is triphenyl phosphonium phosphate. The catalyst is employed as a 30% solution in methanol in an amount which provides 0.45 milliequivalent of catalyst.

^c EtTPhP • HAc is ethyltriphenyl phosphonium acetate • acetic acid complex. The catalyst is employed as a 70% solution in methanol in an amount which provides 0.45 milliequivalent of catalyst.

^d EtTPhP is ethyltriphenyl phosphonium. The catalyst is employed as a 30% solution in methanol in an amount which provides 0.45 milliequivalent of catalyst.

The pre-catalyzed resin data shows that tetramethylene bis triphenyl phosphonium salts are superior catalysts for use in pre-catalyzed epoxy resin compositions. The shelf-life of the pre-catalyzed resins was significantly improved.

Example 5

The procedure of Example 1 was employed except that 350 gms (1.937 equiv.) of a diglycidyl ether of bisphenol A having an EEW of 180.7; 202.8 (1.779 equiv.) of bisphenol A and 0.32 gms (0.86 milliequiv.) of tetramethylene bis(triphenyl phosphonium bromide) were employed. Heating was applied to raise the temperature gradually to 150 °C and the exotherm temperature was 215 °C. The cook temperature was also kept at 215 °C for 4 hours. The product analyses are shown in Table IV.

Comparative Experiment J

The procedure of Example 5 was followed except that 0.30 g (0.86 milliequiv.) of methylene bis(triphenyl phosphonium bromide) was employed as the catalyst. The reaction mixture became extremely viscous at 1.5 hours after exotherm and the reaction was terminated. Product analyses are shown in Table IV.

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Comparative Experiment K

The procedure of Example 5 was followed except that 0.50 gms (0.86 milliequiv.) of a 70 weight percent methanolic solution of ethyl triphenyl phosphonium acetate*acetic acid complex was employed as the catalyst. The product analyses are reported in Table IV.

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TABLE IV

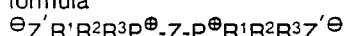
Ex. or Comp. Expt.	Catalyst	Target EEW	EEW	% of Target EEW	Mw	Polydispersity
5	tetramethylene bis (triphenyl phosphonium bromide)	3,500	3,549	101.4	25,252	4.14
J*	methylene bis (triphenyl phosphonium bromide)	3,500	4,172	119.2	47,125	6.03
K*	ethyltriphenyl phosphonium acetate* acetic acid complex	3,500	3,233	92.37	20,761	3.69

*Not an example of the present invention.

The data in Table IV shows that tetramethylene bis (triphenyl phosphonium bromide), Example 5, is an excellent catalyst for epoxy resin advancement. Using tetramethylene bis(triphenyl phosphonium bromide) as the catalyst for epoxy resin advancement, the targeted EEW is reached even when the reaction is carried out at high temperatures, whereas when using conventional catalysts like ethyl triphenyl phosphonium acetate*acetic acid complex, Comp. Expt. K, the conventional catalysts are prematurely deactivated, resulting in incomplete reaction, i.e. an EEW lower than the targeted EEW is reached. On the other hand, the methylene bis (triphenyl phosphonium bromide) catalyst, Comp. Expt. J, does not become deactivated, resulting in very high EEW, broad M.W. distribution and uncontrollable viscosity build due to continuing side-reactions.

Claims

1. A precatalyzed composition comprising an epoxy-containing compound having at least one vicinal epoxy group per molecule and a catalyst having two phosphonium groups per molecule represented by the formula



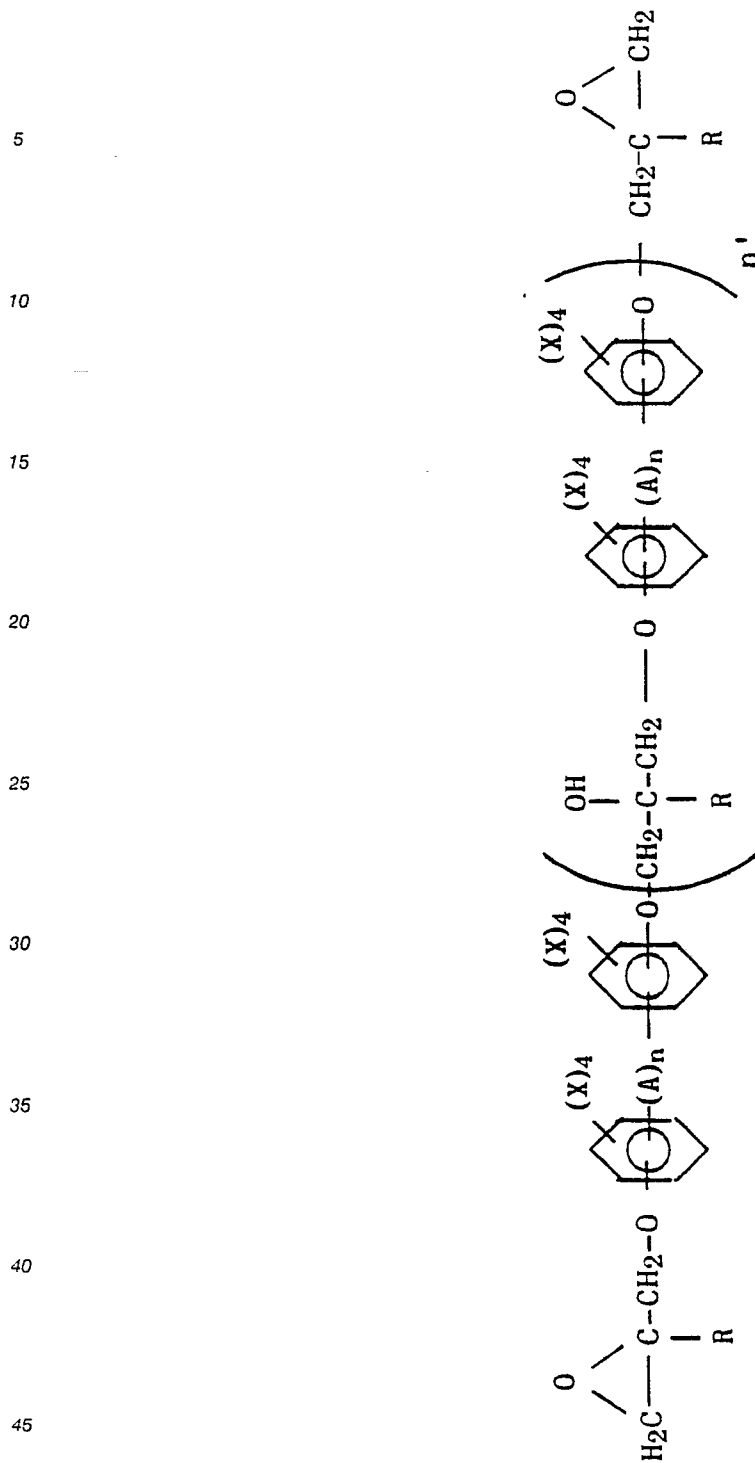
wherein each R^1 , R^2 and R^3 is independently an aromatic group or an inertly substituted aromatic group; Z is $-(C(R^4))_2(a)-$; each R^4 is independently hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms; Z' is any suitable anion; a has a value of at least 4; and wherein the catalyst is present in an amount of from 0.0005 to 50 milliequivalents per epoxide equivalent of the epoxy-containing compound.

2. A precatalyzed composition of Claim 1 wherein each R^4 is independently hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms; Z' is a halide, phosphate, bisphenate or a carboxylate*carboxylic acid complex; a has a value from 4 to 20; and the catalyst is present in an amount of from 0.05 to 30 milliequivalents per epoxide equivalent of the epoxy-containing compound.

3. A precatalyzed composition of Claim 2 wherein each R^4 is hydrogen; Z' is bromide; and a has a value from 4 to 6; and the catalyst is present in an amount of from 0.5 to 10 milliequivalents per epoxide equivalent of the epoxy-containing compound.

4. A precatalyzed composition of Claim 3 wherein said catalyst is tetramethylene bis(triphenyl phosphonium bromide), pentamethylene bis(triphenyl phosphonium bromide), or a combination thereof.

5. A precatalyzed composition of Claim 1 wherein said epoxy-containing compound having at least one vicinal epoxy group per molecule is an epoxy resin represented by the following formula



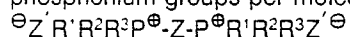
50 wherein A is a divalent hydrocarbyl group having from 1 to 12 carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; each X is independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having from 1 to 12 carbon atoms, or a halogen; n has a value of zero or 1 and n' has a value from zero to 0.5.

6. A precatalyzed composition of Claim 5 wherein each R is hydrogen; each X is independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having from 1 to 4 carbon atoms, chlorine or bromine; n has a value of 1 and n' has a value from 0.1 to 0.3.

7. A precatalyzed composition of Claim 6 wherein said epoxy-containing compound having at least one vicinal epoxy group per molecule is a diglycidyl ether of bisphenol A.

8. A process for reacting an epoxy-containing compound having at least one vicinal epoxy group per

molecule with an acidic compound in the presence of a catalytic quantity of a catalyst having the phosphonium groups per molecule represented by the formula



wherein each R^1 , R^2 and R^3 is independently an aromatic group or an inertly substituted aromatic group; Z is $-(C(R^4))_a-$; each R^4 is independently hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms; Z' is any suitable anion; and a has a value of at least 4.

9. A process of Claim 8 wherein each R^4 is independently hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms; Z' is a halide, phosphate, bisphenate or a carboxylate*carboxylic acid complex; a has a value from 4 to 20; and the catalyst is present in an amount of from 0.0005 to 50 milliequivalents per epoxide equivalent of the epoxy-containing compound.

10. A process of Claim 9 wherein each R^4 is hydrogen; Z' is bromide; and a has a value from 4 to 6; and the catalyst is present in an amount of from 0.5 to 10 milliequivalents per epoxide equivalent of the epoxy-containing compound.

11. A process of Claim 10 wherein said catalyst is tetramethylene bis(triphenyl phosphonium bromide), pentamethylene bis(triphenyl phosphonium bromide), or a combination thereof.

12. A process of Claim 10 wherein said epoxy-containing compound having at least one vicinal epoxy group per molecule is an epoxy resin represented by the following formula

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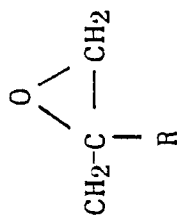
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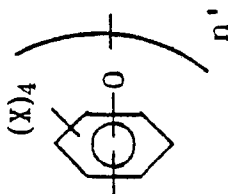
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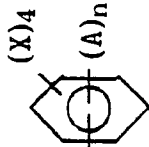
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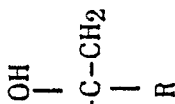
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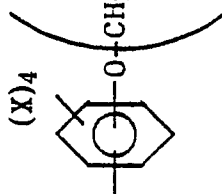
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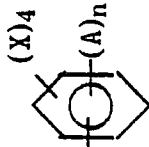
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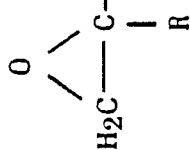
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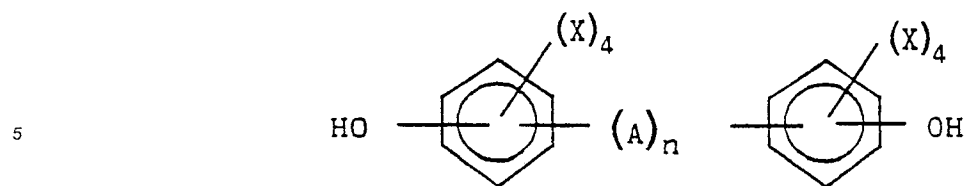


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50 wherein A is a divalent hydrocarbyl group having from 1 to 12 carbon atoms; each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; each X is independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having from 1 to 12, carbon atoms, or a halogen; n has a value of zero or 1 and n' has a value from zero to 0.5; said acidic compound is a phenolic hydroxyl containing compound represented by the following formula

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wherein A, X and n is as previously defined.

10 13. A process of Claim 12 wherein each R is independently hydrogen or methyl; each X is independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having from 1 to 6 carbon atoms or a halogen; n has a value of zero or 1 and n' has a value from 0.1 to 0.4.

14. A process of Claim 13 wherein each R is hydrogen; each X is independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having from 1 to 4 carbon atoms, chlorine or bromine; n has a value
15 of 1 and n' has a value from 0.1 to 0.3.

15. A process of Claim 14 wherein said epoxy-containing compound having at least one vicinal epoxygroup per molecule is a diglycidyl ether of bisphenol A and said compound having at least one phenolic hydroxyl group per molecule is bisphenol A.

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